



## Rapid communication

## In situ synthesis of cobalt alginate/ammonium perchlorate composite and its low temperature decomposition performance



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## ABSTRACT

To prevent from agglomeration of nano-catalysts, the idea of in situ synthesis was applied to study on thermal decomposition of ammonium perchlorate (AP). Herein, we reported a feasible approach to prepare cobalt alginate/ammonium perchlorate (CA/AP) composite by ionic crosslinking solidification method and the catalytic performance on the thermal decomposition of AP was investigated. The surface morphology and composition of samples were characterized by SEM, EDS, XRD, FT-IR and XPS. Also, the catalytic thermal decomposition of AP was characterized by DSC. The thermal decomposition temperatures of composite prepared by 2, 4, 6 and 8 wt%  $\text{Co}(\text{NO}_3)_2$  which were respectively decreased in the exothermic peak of AP by 79.0, 89.8, 89.3 and 92.7 °C. In a word, all the results indicated that CA/AP composite could lower the decomposition temperature due to not agglomeration. Therefore, CA/AP composite shows a broad application prospects in the field of AP-based propellant.

## 1. Introduction

As we all know, ammonium perchlorate (AP) is one of the major component of composite solid propellants. The performance of composite solid propellants depends on the thermal decomposition of AP. By using additives as catalysts, it can improve the combustion behavior of the solid propellant, lower the thermal decomposition temperature of AP, and increase the released heat [1]. Up to now, many studies have been carried out on the thermal decomposition of AP by adding kinds of catalysts, such as metal oxides  $\text{Co}_3\text{O}_4$  [2],  $\text{CuO}$  [3],  $\text{CoO}$  [4],  $\text{ZnO}$  [5],  $\text{Fe}_2\text{O}_3$  [6]. Recently there has been widely a hot research topic in nanometas and their oxides as nano-catalysts, which have reduced dimensions, high surface activity, and high catalytic performances [7]. However, nano-catalysts are likely to agglomerate and uneven distribution to reduce surface active sites due to their small size and large surface area [8]. In order to prevent from these phenomena, in situ synthesis of new catalysts has a strong tendency on the thermal decomposition of AP [9–11].

Sodium alginate (SA) is a natural polysaccharide extracted from brown seaweeds. Its linear chain structure is composed of  $\alpha$ -1,4-L-guluronic acid (G) and  $\beta$ -1,4-D-manuronic acid (M) [12]. It can easily be combined with some multivalent metal cations forming stable gel in the water solution. Due to sodium alginate (SA), which can easily be combined with some multivalent metal cations forming stable gels in the water solution, and also its unique biodegradability, biocompat-

ibility, hydrophilicity, lowcost and nontoxicity, SA has been widely used in food, drug delivery system, agriculture, biological and daily chemicals industry [12–16]. Nevertheless, there are very few reports about applications in solid propellants. Cobalt compounds exhibit remarkable catalytic effects on the thermal decomposition of AP [11,17,18]. In this work, to prevent nano-catalysts from agglomerating easily, we designed a feasible and attractive approach to continuously prepare in situ synthesis of cobalt alginate/ammonium perchlorate (CA/AP) composite by combining the interaction between SA and  $\text{Co}^{2+}$ . Moreover, we investigated the effect of different cobalt ion concentrations on the catalytic thermal decomposition of AP. As expected, in situ synthesis of CA can remarkably enhance the catalytic effect and accelerate the thermal decomposition of AP.

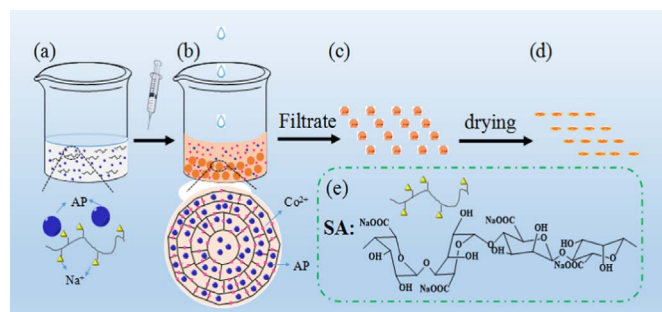
## 2. Materials and methods

## 2.1. Materials

Sodium Alginate (SA) and Cobaltous Nitrate Hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) with analytically pure were purchased from Chengdu Kelon Chemical Reagent Factory. Ammonium Perchlorate (AP, AR) was provided by Aladdin (Shanghai, China).

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**Fig. 1.** (a–d) The formation process diagram of CA/AP composite and (e) chemical structure of Sodium Alginate (SA) . .

## 2.2. Preparation of CA/AP composite

The samples were prepared by dripping method and ionic cross-linking solidification method. The formation process diagram was shown in Fig. 1.

First, AP and SA with mass ratio of 93:7 were added into distilled water to obtain a homogeneous solution (Fig. 1a). Then, a series of  $\text{Co}(\text{NO}_3)_2$  solution with different concentrations (2, 4, 6 and 8 wt%) were prepared, and pure AP was dissolved in different concentrations of  $\text{Co}(\text{NO}_3)_2$  solution until saturated state. Finally, the mixture solution of AP and SA was separately dripped into different concentrations of  $\text{Co}(\text{NO}_3)_2$  solution by using a syringe (Fig. 1b). They were precipitated to form composite gels in  $\text{Co}(\text{NO}_3)_2$  solution due to ionic crosslinking. The mixture solution was solidified for 30 min. After that, the CA/AP composite was obtained, and was washed with distilled water for two times (Fig. 1c). Then the samples were dried in vacuum oven at 40 °C for 24 h. The final samples were obtained (Fig. 1d).

## 2.3. Testing methods

The surface morphology, structure and composition of the samples were analyzed by scanning electron microscopy (SEM, Ultra-55, Carl Zeiss, Germany), equipped with energy dispersion X-ray spectrometer (EDS) and operated at an acceleration voltage of 10 kV for 50 s. X-ray diffraction (XRD, X' Pert pro, Panacco, Netherlands) was carried out on Bruker D8-Advance diffractometer equipment with Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm). The sample was scanned in the  $2\theta$  range from 10° to 80°. Fourier transform infrared (FT-IR) spectra was measured on a Nicolet-5700 FTIR spectrometer using pressed KBr pellets. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 electron spectrometer using Al K $\alpha$  irradiation.

The catalytic effect of prepared samples on the thermal decomposition of AP was observed by differential scanning calorimetry (DSC-131, Seata Corporation, France) at a heating rate of 10 °C min<sup>-1</sup>, in a temperature range of 30–500 °C and under nitrogen with the flow rate of 30 mL min<sup>-1</sup>. The approximate mass of samples was 0.8 mg in all runs.

## 3. Results and discussion

### 3.1. The surface morphology, structure and composition of CA/AP composite

As shown in Fig. 2a, forming CA/AP composite was with elasticity, smooth surface and regular shape, size, as well as strength before drying. However, CA/AP composite was investigated after drying in vacuum oven at 40 °C for 24 h (Fig. 2b). There was obvious rough and uneven wrinkles for composite on its surface, which could be caused by the partial collapsing of polymer network during drying [18]. More specifically, by SEM images (Fig. 2c), the surface of CA/AP composite showed a denser morphology. We deduced that this might be because a

large amount of AP was coated with CA to form a dense coating. To further confirm that the elemental distribution of CA/AP composite, the EDS mapping analysis was used to determine the composition of samples. The composition analysis results were shown in Fig. 2(d–f) and indicated that Co, O, and Cl were well dispersed in the composite, which indicated that CA and AP were evenly distributed in the composite. Consequently, this structure might prevent from agglomeration phenomena and ensure the most efficient catalytic activities. In addition, to gain more insight, we conducted several XRD, FT-IR and XPS studies.

Fig. 3a showed the X-ray diffraction (XRD) pattern of CA washed AP in CA/AP composite. Clearly, the XRD pattern of the prepared sample indicated an amorphous structure [19,20]. The broad diffraction peak was detected at approximately 22°, which were similar to those reported for CA [19,21]. Furthermore, the structures of the SA and CA were observed by fourier transform infrared (FT-IR) spectroscopy. As shown in Fig. 3b, The strong bands at 1637.10 and 1616.60 cm<sup>-1</sup> in the spectrum of SA were attributed to the asymmetric stretching of carboxyl groups. Also, the peak at 1383.61 cm<sup>-1</sup> corresponded to symmetric stretching vibration of carboxyl groups of SA. As divalent cobalt ions replaced sodium ions in the SA, there were obvious shifts to lower wavenumbers in the asymmetric vibrations of carboxyl groups and higher wavenumber in the symmetric vibrations of carboxyl groups. For similar band shifts, there were also reported [21,22].

To further confirm the elemental composition and electronic structure of CA, X-ray photoelectron spectroscopy (XPS) measurements were determined in the region of 0–1200 eV. As shown in Fig. 3c, C 1s, O 1s, and Co 2p were observed from the XPS survey spectrum, respectively. This result demonstrated that C, O and Co elements existed in the CA sample. Further, Fig. 3d showed high-resolution XPS spectrum of the Co 2p. Two peaks located at 780.90 and 798.38 eV were detected, respectively, which were corresponded to the Co 2p<sub>1/2</sub> and Co 2p<sub>3/2</sub> binding energies [19,21]. This was ascribed to the characteristic of surface Co(II) species. Thus, the XPS results also confirmed the existence of Co element, and Na<sup>+</sup> was substituted by Co<sup>2+</sup> to form CA.

### 3.2. The catalytic activity determination

The thermal decomposition performance of composite prepared by different concentrations of  $\text{Co}(\text{NO}_3)_2$  was determined by DSC measurements. As shown in Fig. 4, it could be seen that all DSC curves indicated an endothermic peak in the range of 245–248 °C due to crystallographic transition. In curve of pure AP, it had two exothermic peaks at 312.7 °C and 418.4 °C. It was because low temperature process was partial decomposition and high temperature process was complete decomposition. Compared to AP, the SA/AP composite showed a lower decomposition temperature, but the catalytic effect was not obvious. However, the exothermic peaks of composite prepared by 2, 4, 6 and 8 wt%  $\text{Co}(\text{NO}_3)_2$  respectively located at about 339.4, 328.6, 329.1 and 325.7 °C (decreased by 79.0, 89.8, 89.3 and 92.7 °C). With concentration of  $\text{Co}(\text{NO}_3)_2$  increased, the decomposition temperature was gradually decreased. In a word, based on the above all results, we confirmed that CA was a good catalyst for the thermal decomposition of AP by in situ synthesis.

### 3.3. Catalytic mechanism of thermal decomposition of AP

As we all know, AP is the most common oxidant in composite solid propellants. But, up to now, the mechanism of thermal decomposition of AP is not still fully understood due to this process is a complex hetero-phase reaction process which contains several reactions in the solid, adsorbed and gaseous phases [18]. According to lots of literature, cobalt compounds have shown good catalytic activities on thermal decomposition of AP. Due to the solubility of SA and AP in water, SA and AP in the bonded SA/AP composite can be evenly mixed in

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